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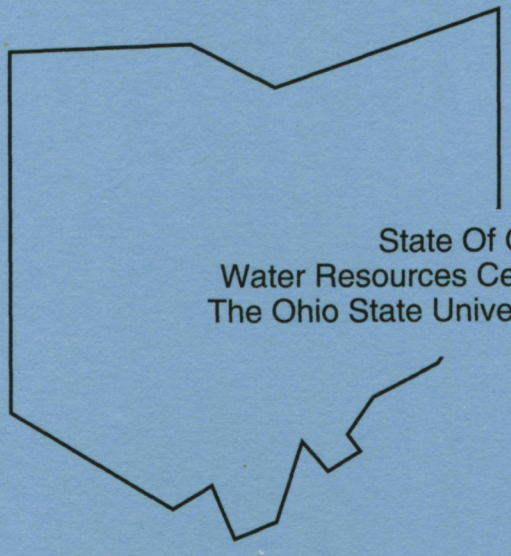
Report No. G-2039-04

FISCAL YEAR 1993 PROGRAM REPORT

Robert C. Stiefel
Director

United States
Geological Survey



State Of Ohio
Water Resources Center
The Ohio State University

Report No.
G-2039-04

Fiscal Year 1993 Program Report
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Geological Survey

by

Ohio Water Resources Center
The Ohio State University
Columbus, Ohio 43210

Robert C. Stiefel, Director

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ABSTRACT

Most of Ohio's water problems are associated with water quality. Of primary concern are the sediments, nutrients and acids in the surface waters from urban, agricultural and mining areas, and the toxic and hazardous wastes that threaten the ground and surface waters. The focus of the 1993 State Water Research Program was directed at these areas. The research and technology transfer program consisted of the following activities: The technology transfer programs of the Water Resources Center continues to disseminate information about the water resources of Ohio to the local and state decision-makers. It also provides technical assistance to help resolve some of the state's major water problems. One project was an oceanographic dynamics study, for Lake Erie, which used mathematical models to calculate how contaminant loading from rivers will interact with the Great Lakes Forecasting System. This project will provide accurate and timely loading figures for the forecasting system. The natural quantities of uranium and thorium in 169 of Ohio's aquifers has been research by Gerald Matisoff, to learn how these amounts compare to new legislative standards. One project researched a comprehensive study of the behavior of organically-complexed metals in solutions comprised of aqueous and nonaqueous solvents. This information will apply to proposed remediation strategies for contaminated soils that use washing techniques to remove nonpolar organic contaminants. Another project studied the quantitative structure-activity relationships for predicting the fate and effects of pesticides. Another researcher studied the use of alkaline flue gas desulfurization byproducts to reclaim acidic abandoned minespoil in eastern Ohio and as a substitute for limestone in agricultural production.

Training on these research projects was provided to six students from five disciplines at two universities. These include two M. S. students in the fields of Environmental Science and Agronomy; three Ph.. D. students in the fields of Civil Engineering, Environmental Science and Geological Science. A Post Ph. D. researcher in Environmental Science was also trained under this project.

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Water Problems and Issues of Ohio

Water is one of Ohio's most important natural resources. Bounded on the north by Lake Erie and on the south by the Ohio River and containing other extensive ground and surface waters, Ohio has an adequate supply of water to meet its immediate needs. However, the combination of large, heavily industrialized urban centers; extensive agricultural activities; high volume coal production and large coal reserves; and the associated demands for new energy production continues to cause concerns related to water quality and water management. In addition, extreme hydrologic events cause localized problems of both excessive water and water deficiencies at times.

Surface Water

The northern 25 percent of Ohio's area drains into Lake Erie, while the southern portion drains into the Ohio River. Runoff from Ohio's streams and rivers averages about 25 billion gallons per day. The state also receives nearly a billion gallons of runoff daily which drains through the Maumee River to Lake Erie from the neighboring state of Indiana; and Ohio has access to additional flows past its boundaries in Lake Erie and the Ohio River that total well over 150 billion gallons of water per day.

Last year, more than 16 billion gallons of water were withdrawn from Ohio's surface sources each day to meet the demands for municipal supplies; rural needs for domestic and livestock purposes; irrigation; and self-supplied industrial needs including cooling water for thermo-electric power generation. These demands account for only 60 percent of the available surface waters in the state's streams each day, and localized shortages only develop during certain dry seasons and periodic droughts.

The combined length of all the streams in Ohio approaches 44,000 miles, which means that there is approximately one mile of stream for each square mile of surface area in the state. In addition, there are more than 50,000 lakes, ponds and reservoirs within the state having a combined surface area of 200,000 acres. Only a small fraction of these, about 6,700 acres, occur naturally. The remainder are man-made impoundments that range in size from small farm ponds to large multipurpose reservoirs.

The reservoirs in the state are used to provide water for many different purposes including municipal, agricultural and industrial supplies; stream flow augmentation; flood control; and recreation. No impoundments in Ohio, other than those on the main stem of the Ohio River, provide water for downstream navigation or hydro-electric power generation. However,

there is extensive navigation on both Lake Erie and the Ohio River, and consideration is being given to the installation of low-head hydro-electric generators at several developed dam sites throughout the state.

Flooding, still a major problem in Ohio, affects both urban and agricultural areas; and it has been estimated that nearly two million acres of land in Ohio are flood prone. This represents over seven percent of the total area of the state and includes nearly four percent of those areas classified as urban regions. Average annual flood damages in Ohio vary from year-to-year but amount to several millions of dollars annually.

Ground Water

Ground water is an important part of Ohio's water resources. Ground water underlies most of the state but is predominant in the glacial drift in the northwest, in the ice-contact and outwash deposits in river valleys along the border of the glaciated areas, and in the bedrock of the western portions of the state. Ground water supplies are largest in the glacial valley-train deposits in those drainage basins which border the Ohio River including the Ohio, Miami, Little Miami, Scioto, Hocking and Muskingum Rivers. Well yields from these deposits often exceed 500 gallons per minute (gpm), while aquifers in the glacial drift in the northwest and west-central parts of the state produce yields between 100 and 500 gpm. Isolated aquifers in the northeast, northwest and southwest have yields between 25 and 200 gpm, while much of the northeast contains aquifers whose yield is between 5 and 25 gpm. With the exception of the valleys along the major streams, most of the aquifers in the area that is tributary to the Ohio River have yields less than 5 gpm.

Three-quarters of Ohio's 650 public water supply systems use ground water as their source. In terms of volume withdrawn, however, a lesser share of these supplies comes from ground water, for only around a half billion gallons of ground water are withdrawn each day for public water supply purposes, while over one billion gallons come from surface water sources. However, ground water supplies nearly 80 percent of the rural water needs in Ohio, 32 percent of the irrigation waters and 21 percent of the industrial water demands. Nearly one billion gallons of ground water are withdrawn in the state each day to meet these needs.

Water Quality

It is the quality of water, rather than its quantity, that is the more critical and limiting condition associated with the use of both ground and surface waters in Ohio. The ground waters of the state frequently have relatively high, natural mineral contents; but, except for a few local areas, most of these waters are free from man-related contamination. Most complaints are related to increased levels of turbidity, bacterial populations and other substances from improperly sited or poorly constructed or maintained wells. Other problems

are related to the spillage and leakage of brines and petroleum at oil wells in the southeastern part of the state; the mis-application of pesticides, herbicides and insecticides in agricultural areas; and the improper siting and operation of solid and liquid waste disposal facilities. Some minor ground water problems associated with the excessive use of highway de-icing salts or its improper storage have also been reported.

The dissolved solids concentrations in Ohio's streams range between 120 and 2,500 milligrams per liter (mg/l). The higher concentrations are found in the Tuscarawas, Cuyahoga and Grand Rivers and in other stream reaches below major municipal and industrial outfalls or in areas subjected to diffuse source runoff.

Of the 23,000 miles of the principal rivers downstream of major urban areas in the state that have been monitored, 16,000 miles, or 70 per cent of these streams, meet the current water quality standards. Where problems do exist, they are frequently caused by inadequate municipal wastewater treatment at facilities that need be upgraded or expanded, or by combined sewer overflows. Substantial improvements in surface water quality have resulted from the development of pretreatment regulations for industrial waste discharges to municipal sewerage systems. Violations of the state's water quality standards occur most often in dissolved oxygen levels; ammonia nitrogen concentrations; the numbers of fecal coliforms; and the levels of heavy metals such as lead, zinc, and cadmium.

Acid mine drainage is a major cause of water quality problems throughout the Appalachian Coal Basin in the eastern United States. In Ohio this region extends in a band approximately 50 miles wide in a southwesterly direction from the east-central to the south-central parts of the state. Acid drainage from abandoned and improperly operated or reclaimed coal mined lands causes a loss of water for domestic and industrial uses; the degradation of water quality for recreational purposes; a lethal impact on the aquatic life in a stream; and an accelerated deterioration of highway and railroad bridges and electrical transmission lines and towers. Drainage from abandoned coal mines, both surface and underground, has impacted around 1,500 miles of streams in 27 counties in southeastern Ohio. Approximately 370,000 acres of abandoned strip mines, 7,000 acres of coal refuse piles and 3,000 underground mines are contributing to this problem. It has been estimated that four billion dollars would be needed to reclaim the abandoned mines and refuse piles throughout Ohio. Projected revenues from severance taxes earmarked for abandoned mine reclamation come to about ten million dollars annually. Obviously, the technologic problems and the economic costs associated with the control of acid mine drainage will continue to keep this a major problem of water quality in southeastern Ohio for years to come.

Little detailed information is available concerning the impacts that diffuse sources of pollution such as agricultural and urban stormwater drainage have on the quality of water in Ohio's inland streams. One concern with non-point pollution is the sediment that is dislodged from the land surface and carried to the streams. Of greater concern are the pollutants, such as the

nutrients, heavy metals and toxic organic substances, that enter the streams attached to the sediments. No need for intensive, non-point source control programs to meet water quality standards in that area of the state that drains to the Ohio River has been shown; but several studies are underway in the Lake Erie drainage basin to define the role of agricultural drainage on the water quality in the lake. Much more research and many more demonstration projects on the best management practices for agriculture, silviculture, mining and urban runoff control must be conducted before this problem is fully understood and control measures can be instituted.

The trophic status of several lakes and reservoirs has been studied; and the results suggest that the lakes and reservoirs in the sandstone bedrock areas of the state have generally lower trophic levels than those in the limestone bedrock areas or glaciated regions. Water quality was generally good to excellent in most of the lakes and reservoirs surveyed. However, excessive concentrations of copper and other heavy metals, bacteria and other pollutants normally associated with urban activities were identified in some of the lakes. Recent studies on Lake Erie indicate that there has been a reduction in several key pollutants and a gradual, but steady, improvement in the water quality in the Lake during the past few years. Phosphorus is a major pollutant which results in the excessive growth of algae and other aquatic plants. As these plants die and decay, they deplete the oxygen resources of the Lake. The construction of facilities to remove phosphorus at those municipal wastewater treatment plants which discharge directly to Lake Erie has been a major factor in the reduction of phosphorus loadings and of the subsequent reduction of the anoxic areas within the Lake. Additional work on the control of phosphorus from both diffuse sources and point sources needs be accomplished, but a significant start has been made.

Levels of bacteria have been reduced in the nearshore zones where municipal wastewater treatment facilities have been constructed. This has permitted regulatory agencies to re-open bathing beaches which were often closed during the period between 1960 and 1970. Concentrations of mercury and pesticides have been reduced substantially, principally because of the federal bans that have been instituted on their manufacture, use and disposal. PCB remains a major challenge, as does the control of sediment and the nutrients, fertilizers and organic chemicals that are attached to it.

Fish populations, including the walleye pike, are beginning to increase again in the lake; but the quality and diversity of fish is still far from what they were in the past. Thermal pollution is a localized problem in some near-shore areas. However, as closed cycle cooling is required on all power generation facilities, the extent of this problem will diminish.

PROGRAM GOALS AND PRIORITIES

The Water Resources Center at The Ohio State University encourages and supports research that is directed at providing information needed to solve the major water problems at the local, state, regional and national levels. The research program at the Center includes basic or fundamental research, problem oriented or applied research, and information dissemination and technology transfer activities.

During FY 1982, the Center, in cooperation with several groups of water-related agencies and officials throughout the State prepared a prioritized list of Ohio's major water resources problems. Based upon this analysis, the following ranking of these problems was developed:

1. **POLLUTION FROM DIFFUSE SOURCES** - including agricultural runoff; urban runoff; runoff from on-site waste disposal systems; runoff from active, reclaimed or abandoned coal and strip mines.

2. **CONTAMINATION OF DRINKING WATER SUPPLIES** - including surface and ground waters for both urban and rural uses by diffuse and point sources, and by the disposal of toxic and hazardous wastes on the land.

3. **TOXIC AND HAZARDOUS WASTE DISPOSAL** - including their control, treatment, disposal and impact upon land, water and air resources.

4. **POLLUTION FROM POINT SOURCES** - including municipal and industrial sources not yet in compliance with their NPDES permits.

5. **IMPACTS OF FLOODING AND DRAINAGE** - including flood damages, the use of flood plains and alternative structural and non-structural means of controlling floods and reducing flood damages.

6. **IMPACTS OF WATER RESOURCES DEVELOPMENTS** - including the impacts on various developments such as the extension of water mains and sewers into rural areas; flood control projects; hydro-electric power generation; water -based recreation; etc.

7. **INSTREAM FLOWS NEEDS** - including interrelationships among water quality, water quantity and land use practices on the instream flow needs for fish, wildlife, recreation and the optimum development and protection of these instream uses.

8. **IMPACTS OF SYNTHETIC FUEL DEVELOPMENT** - including requirements for water and impacts of the disposal of wastes from these processes into water and onto the land.

9. **IMPACTS OF ATMOSPHERIC POLLUTION** - including the effects of acid precipitation and atmospheric fallout on water quality and the environment.

10. **ALLOCATION OF WATER RESOURCES-** including the development of contingency plans for the allocation and conservation of limited water supplies among competing water users during periods of low stream flows.

Subsequently, the Directors of the Water Resources Research Institutes in the Great Lakes, Upper Mississippi and Ohio River Basin's met to identify from their State problems the major water resources research priorities for the Region. A listing of these priorities is included at the end of this Section of this Report.

The focus of the 1993 State Water Resources Research Program was primarily directed at some of these critical needs. The technology transfer programs of the Water Resources Center continue to disseminate information about the water resources of Ohio to the local and state decision-makers, and provides technical assistance to help resolve some of the state's major water problems.

The project by Keith W. Bedford was an oceanographic dynamics study, using mathematical models to calculate how contaminant loading from rivers during and immediately after storms will interact with the Great Lakes Forecasting System. This project entitled "A Nearshore Coliform Prediction and Forecasting System for CSO Hazard Warning" will provide accurate and timely loading figures for the study.

The research by Gerald Matisoff of Case Western Reserve University on "Radium and Uranium Chemistry and Transport in Ohio Major Ground Water Aquifers", developed a technique for analyzing the natural radioactive substances in groundwater and conducted a state-wide survey of their concentrations in the major water supply aquifers. This year researchers studied the amounts of uranium and thorium naturally found in 169 of Ohio's aquifers.

"The Effects of Cosolvent Mixtures on the Environmental Chemistry of Metal-Ligand Complexes" was studied by Professors Samuel J. Traina and John W. Olesik of Ohio State. This research is a comprehensive study of the behavior of organically-complexed metals in solutions comprised of aqueous and nonaqueous solvents. This information will be directly applicable to proposed remediation strategies for contaminated soils that employ solvent washing techniques to remove nonpolar organic contaminants.

Professor Susan W. Fisher, an entomologist, was the principal investigator for "Prediction of Toxicity for Pesticides Found in Ohio Surface Waters". This study advances the knowledge of quantitative structure-activity relationships for predicting the fate and effects of pesticides. This knowledge will greatly improve our ability to predict under which conditions pesticides that are released into the watershed will have an anomalous effect.

The research by Professor Terry Logan, was "The Solubility and Potential for Water Contamination of Arsenic in Coal Combustion Wastes When Used for Coal Mine Reclamation". This study used the alkaline flue gas desulfurization byproducts to understand if they could be used to reclaim acidic abandoned minespoil.

The technology transfer program continued to work closely with the water professionals throughout the state and nation in cooperative efforts, jointly sponsored programs, newsletters and reports. The Ohio Water Education Program, OWEP, provides current information on all water education activities in Ohio and helps teachers network. It also provides K-12 water resources education through Project WET. Ohio State has the lead in a seven state pilot project with the Department of Energy, on environmental management and restoration of DOE sites.

SYNOPSIS

Project Number: 02

Start: July 1993 (Actual)
End: June 1994 (Expected)

Title: A Nearshore Coliform Prediction and Forecasting System for CSO Hazard Warning

Investigator: Dr. Keith W. Bedford, The Ohio State University, Columbus, Ohio

Focus Categories: CP, MOD, ST, WQL

Congressional District: 15

Descriptors: transports, forecasting, tributary loading, numerical modeling, Great Lakes

Problems and research objectives: Nonpoint source watershed runoff from agricultural lands is especially aggravated during storms. With storms occurring roughly every seven to ten days in Ohio (Irish and Platzman [9]), the resulting delivery of these runoff pollutant products to the tributaries, and ultimately the Great Lakes (Erie), is a continuous series of sharp impulsive loads to the Lake. The storm driven loads often occur very quickly, coinciding with the maximum tributary discharges, while the post-storm recession is stretched over time as pollutants are slowly released back to the tributaries from flooded wetlands, etc. In determining the ultimate load to the Lake it is also necessary to account for the effects of strong stratification and water level fluctuations at the confluences (Lee and Bedford [10]). The International Joint Commission (IJC) has designated over forty highly polluted Areas of Concern (AOC), some six of which are the major tributaries draining to Lake Erie. A consortium of the International Joint Commission, USEPA , Canadian Ministry of the Environment and USGS bureaus is charged with the responsibility of estimating these loads to the Great Lakes on a monthly basis. These agencies then in turn must use these data to implement water quality management decisions and remediation plans. The currently used operational load estimation procedure uses monthly average estimates based on empirically adjusted data collected quite far upstream at USGS monitoring sites. These sites are well upstream of the Lake confluence. The Maumee River gauge is over 30 km upstream. The data collected are so far upstream that all the AOC effects are ignored, and one month averaging horizons effectively preclude resolution of the impulsive, spiky nature of the loading. In essence then, accurate loading estimates are not available; the magnitudes are heavily underestimated; and transformations within the downstream tributary/Lake mixing zone in the AOCs are unaccounted for. The result is poor long term water quality management.

In the case of nonconsevative pollutants, such as fecal coliform bacteria, coastal trajectories of pollutant plumes are more important to water quality managers than monthly loadings. Combined sewer overflows lead to plumes of fecal coliform bacteria that present a hazard to coastal populations and cause a general degradation of the coastal environment. These plumes are short lived but dangerous. Locations of land fall and plume path can help in real-time release planning and in the

long term planning for remediation. The Northeast Ohio Regional Sewer District (NEORSD) is responsible for remediating the persistent combined sewer overflows (CSO's) in the Cuyahoga River, the main tributary in the Cleveland area. To design the most cost-effective system, NEORSD needs to know the effect of various water treatment scenarios on the water quality of Lake Erie and particularly the highly used recreational regions around Cleveland. To account for plume trajectories in the coastal region an approach was devised and tested using the historical data base constructed by Great Lakes Forecasting System (GLFS)(Bedford [3]).

Methodology: The vertical plane modeling technology has been adapted to the Maumee River (Podber [13]) and evaluated with known data on the interactions of flow reversals and stratification (Podber and Bedford [14]), as the first step in this two year project. Various combinations of the major factors affecting loading have been tested. These factors include tributary and receiving water temperatures, river transport and stage, lake oscillations and river basin bathymetry (silled and unsilled river bathymetry). The modeling strategy is predicated on the tributaries being relatively narrow and long which for Lake Erie is the case for all of the tributaries except Sandusky Bay. These confluences exhibit significant interactions between vertical stratification and internal and surface, long period oscillations which impede Lakeward transport (Bedford and Mark [1]) and must be accounted for in the model.

Calculations of the horizontal and vertical velocity are made as well as calculations of temperature. A terrain following coordinate system is used which allows full resolution of bathymetry and channel geometry features. While this model is used to calculate a vertically resolved flow in the dredged channel portions, river stage and transport is calculated using the one-dimensional Dynamic Water Quality Model (Bedford et al. [2]) which is now the model in use for all such calculations by the US Army Corps. of Engineers.

To study the coastal processes, the 20-year database constructed by GLFS for NEORSD (Bedford [3]) was used to drive a high resolution version (1~km) of the Great Lakes Forecasting System's hydrodynamic model. After studying the 20 years of storms and Lake responses, two representative storms were chosen for analysis. River loads of fecal coliform bacteria were constructed to estimate different treatment and containment strategies. The domain for the model is 45 km of Lake Erie coastline that encompasses the Cleveland area, the region of concern for NEORSD. A one way nested grid approach is used to initialize and calculate a high resolution velocity and temperature field for the region.

Load estimates are provided to the nested grid model for the Cuyahoga River so that load trajectories can be calculated for the storm scenarios tested. The model used for the Cuyahoga loading was a modified version of the Stormwater Wastewater Management Model (SWMM) described in Podber et.al. 1994. The nested grid model provides a 1 km grid mesh with 12 layers in the vertical, thereby providing for a 3-dimensional water quality calculation. The pollutant plume is tracked for 96 hours until decay of the fecal coliform is almost complete. Impacted areas are clearly shown for the storms selected. The NEORSD chose two worst case representative storms for which various treatment

scenarios were tested, including full unremediated release through various remediation strategies based on storm water control strategies.

Principal Findings and Significance: Results reported in [15] include loading estimates based on idealized inputs. The relative effects of the sill in the Maumee River and the temperature induced density difference between the receiving water and the river water were compared. It was found that the density wall that occurred in the spring lead to a 6 percent increase in loading while the absence or presence of a sill had less than a one percent effect. These results apply only to the sill size that is found in the Maumee bathymetry data. Also a result from this study was the discovery and documentation of an important error in the calculation procedure of the Princeton Ocean Circulation Model (POCM) that is the calculation engine used in GLFS, and widely used in the oceanographic community. In most ocean cases the discovered error is small, however in regions of relatively steep slope the errors are appreciable and cause numerical divergence and instability. Nearshore zones in the Great Lakes are precisely the types of places that the effect will be large (see [15] for details).

In addition to the POCM having difficulty with the nearshore zones, it is suspected that the numerical limitations inherent in the terrain following coordinate system used in the POCM, will lead to a poorly resolved thermocline especially in the deeper Great Lakes. Nearshore process will be affected by the existence of a thermocline. Thermoclines setup in the Great Lakes during the summer months due to solar heating. A layer of warm water rests upon a cooler layer and the density difference associated with the temperature difference creates a two layered system which inhibits the exchange of material and momentum. The inhibited mixing that is associated with a thermocline (pycnocline) will lead to higher concentrations of surface loaded material in the upper layer and lower concentrations in the lower layer.

In order to assess the possible alternative approaches, new procedures for modeling the thermocline of the receiving water were investigated. A literature review has been done on the thermocline and its effect on lake circulation. The local effects of the formation and destruction of the thermocline are unresolved by the current modeling strategy, due to the small vertical scales of the phenomenon. A method called continuous dynamic grid adaption has been tested in the atmospheric sciences community by Dietachmayer [5],and Dietachmayer and Droegemeier [4], and Fiedler and Trapp [6]. This method enhances resolution near regions of strong gradients, and that to date has not been used in the Great Lakes. The method will be modified and tested against data and the POCM in Lake Ontario.

Also improved methods of calculating turbulence closure will be examined based on the approaches of Helfand and Labraga [8], Lobocki [12] [11], and Galperin et al. [7].

The tributary model was tested last year, this year's goal was to link the tributary model to the 3-D POCM running under GLFS on the Ohio Supercomputer Center's (OSC) Cray Y-MP supercomputer. The goal was to link the models together in the most simple way that would still preserve the independence. This presented programming challenges, namely to pass data interactively between the two models. Each models would make a time step, then pass information to the other and stay in a

suspended sleep state until notified that data was available for the next time step. This method allows for the tested and calibrated models to interact without being modified, thus insuring the validity of the calculations.

The procedure for coupling has been tested and stands ready, although no linked tested have been performed to date.

Conference Proceedings:

Podber, D.P., and K.W. Bedford, 1993. "Tributary Loading with a Terrain Following Coordinate System", Estuarine and Coastal Modeling III, Waterway, Port, Coastal and Ocean Division, American Society of Civil Engineers, Ed. Malcolm Spauling et al., pp. 475-488.

Podber, D.P., Yen, C.C.,Regenmorter, L., K.W. Bedford and W.H. Wai,1994,"A Nearshore Model for Cleveland CSO Remediation Design Selection", Hydraulic Engineering '94: Proceedings of the 1994 Conference of The Hydraulics Division, American Society of Civil Engineers. Ed. George V. Cotroneo and Ralph R. Rumer, pp. 222-226.

Training:

One Civil Engineering Ph. D. student is working on this project.

SYNOPSIS

Project Number: 04

Start: July 1993 (Actual)
End: June 1995 (Expected)

Title: Effects of Cosolvent Mixtures on the Environmental Chemistry of Metal--Ligand Complexes

Investigator: Dr. Samuel J. Traina and Dr. John W. Olesik, The Ohio State University

Focus Categories: WQL, TS, HYDGEO

Congressional District: 15

Descriptors: heavy-metals, metal-ligand complexes, chelates, methanol, acetone, thermodynamics, analytical chemistry

Problem and Research Objectives: This research studied the effects of aqueous-organic cosolvent mixtures on the environmental chemistry of toxic metal-ligand complexes. Contamination of soils with mixtures of toxic (and in many instances, radioactive) metals, complexing organic ligands, and organic cosolvents, is a problem receiving growing national attention. These mixed contaminant systems are commonly associated with past and current production of nuclear materials for the nuclear power and weapons industries. The most notorious incidents of this pollution occurred at Department of Energy (DOE) sites such as Mound, Fernald and Piketon, Ohio; Hanford, Washington; Oak Ridge, Tennessee; Los Alamos, New Mexico; and Livermore, California (Riley et al., 1992). However, this mixed contamination can occur in other waste environments (landfills, hazardous waste sites, solvent washing of contaminated soils, etc.). Typically this type of contamination results14 from the use of organic solvents containing chelating ligands such as citric acid, oxalic acid and EDTA in the extraction of U and Pu from spent fuel rods.

Clearly, contamination of soils, sediments, and ground water by these complex mixtures is a serious environmental problem. Unfortunately, little is known about the environmental chemistry of metal-organic ligand complexes in aqueous-organic cosolvent solutions. Yet an understanding of this chemistry is considered essential in predicting the fate of these toxic mixtures in surface and subsurface environments (Riley et al., 1992). The problem is further compounded by a general lack of conventional analytical methodologies which can be used to quantify organically- complexed metals in cosolvent solutions. Our research has addressed these deficiencies by adapting existing analytical methodologies (potentiometry, uv-vis spectroscopy and capillary electrophoresis-inductively coupled plasma) to work in these mixed solvent systems. The results of these studies are discussed below. Future activities will be comprised of completion of the methods development and extension of the mixed solvent system to studies of Co-EDTA sorption by model mineral surfaces in methanol-water and acetone-water systems.

Results and Benefits: The results from this research will be multi-fold. Significant gains will be made in the area of environmental analytical chemistry. The development of improved technologies for the quantification of metal-ligand complexes will provide direct benefits to environmental chemists in both aqueous and nonaqueous environments. A comprehensive understanding of the behavior of organically-complexed metals in solutions comprised of aqueous and nonaqueous solvents, will allow us to revise existing geochemical computer codes presently utilized in both exploratory and remediation activities at many contaminated sites. Additionally, studies on the sorption and transport of complexed metals, in mixed solvent systems, will provide important information which can be utilized by soil scientists, hydrogeologists and environmental engineers currently working on the remediation of DOE and DO facilities. Finally, this research will be directly applicable to proposed remediation strategies for contaminated soils that employ solvent washing techniques to remove nonpolar organic contaminants. While such methods can remove the organic contaminants, they could have unexpected effects on toxic metals.

Methodology: To date, research has focussed on the metals, Cu, Co and Pb, the ligands, EDTA, NTA, oxalate and citrate and the mixed solvent systems of methanol-water and acetone-water.

An automatic titrator (Mettler DL 70ES) and an Orion Sure-flow glass electrode were used for all titrations and the stability constants were extracted by computer codes PKAS and BEST [Martell et al]. UV-VIS spectroscopy was used as a reference method and the computer program SQUAD [Leggett] was used to derive the constants from the spectra.

Calibration of the pH Glass Electrode

HCl was used in both aqueous and semi-aqueous solutions to relate the pH meter readings to [H] of the system. The HCl was assumed fully dissociated when the dielectric constant of the solution was > 30. The drift of the electrode was monitored in mixed solvents and the tolerable limit of $\Delta p[H] = 0.01$ before and after a titration series. The temperature was controlled to be within $\pm 0.1°C$ with a thermostated titration vessel and 0.1M $(CH_3)_4NCl$ was used as the supporting electrolyte.

Titration of Metal Ion-ligand Systems

The same conditions were employed as during the electrode calibrations.

Principal findings and significance: Our analytical data shows a general trend of increasing metal-ligand stability constants with increased organic cosolvent content. We found the SQUAD program sometimes has difficulty in refining two or more constants at one time, it may be due to its less efficient iteration routine [Leggett] than that used in PKAS and BEST [Martell et al.], therefore, we utilized constants derived from potentiometry into SQUAD and if the SQUAD converged we considered the constants confirmed by UV-VIS. Agreement was generally within 10 percent for the two analytical methods. Martell and Smith have analyzed the uncertainty, represented by the range, of the constants in water to be about .01 to .2 log unit. In our co-solvent systems, the ranges were generally < .5 log unit. For the acidic constants of the ligands, the pK's higher than p[H] 10 or lower than p[H] 2 are difficult to measure due to poor performance of the glass electrode in these ranges. For the metal-ligand complexes, the closer these constants are to the acidic constants of the ligands, the more precise the titration will be, because the measurement is based on the displacement of the H+ on the ligands by the metal ions. Derby-Huckel theory was used to convert the concentration quotients into activity constants in semi-aqueous solutions and water [Serjeant].

We utilized a matrix analysis method to determine the number of light absorbing species in solutions [Hartley et al]. We used the computer program TRIANG [Hartley et al] for Co and Cu complexes. When we had Co/EDTA ratio equal to two, which implies at least two light absorbing species must be present in the solution (both Co+2 ion and CoEDTA-2 ion absorb light), the calculation showed only one species present. The reason is that when EDTA is added into a Co or Cu solution, the peak position hardly shifts and the change of the peak magnitudes is linear.

Acetone-H_2O Solution

An approximately linear relationship existed between the constants and the mole fraction of acetone and reciprocal of the dielectric constants of the media, respectively. The Born equation was used to interpret the data:

$$LgKa(m)\text{-}LgKa(w) = \frac{Ne}{4.606RT(4\pi\varepsilon 0)}\left(\frac{1}{rH^{+}} + \frac{ZA}{rA} - \frac{ZHA}{rHA}\right)\left(\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_0}\right)$$

Where K_a means activity constant, m and w mixed solvent and water, respectively, N Avagadro's constant, 0 vacuum permeability, r, radius of an ion, Z valence of the ion, and the dielectric constant. Based on the Born equation, the slope of the equation can be positive, negative or close to zero. We did the calculations for the Co-ligand complexes and assumed a radius of 1.4 for H+ ion, which is the size of a water molecule [King], we also assumed the radius for species such as M(II)EDTA-2 equal to that of H2EDTA-2, etc. Then we obtained a set of radii as following (L is EDTA-4):

Ions	H^+	$H_2Citrate^-$	Hcitrate2-	$Citrate^{3-}$	Co^{2+}	$HOxalate^-$	$Oxalate^{2-}$
Radii ()	1.4	1.62	2.72	3.09	5.76	1.12	1.99

Ions	H_3L^-	H_2L^{2-}	HL^{3-}	L^{4-}	H_2NTA^-	$HNTA^{2-}$	NTA^{3-}	$Co(NTA)_2^{4-}$
Radii ()	1.41	2.28	3.81	5.08	1.43	3.2	4.96	9.84

The ion size parameters in water found in literature are listed as follows [Lindsay]:

Ions	H^+	Co^{2+}	$Citrate^{3-}$	$HCitrate^{2-}$	$H_2Citrate^-$
Radii ()	9	6	5	4.5	3.5

The radii of $Co^{2+}$are close and the sequence of the radii for citrate is in qualitative agreement. With the set of the radii known, we used them to estimate the constants for Co-ligand complexes in acetone-H_2O. Since there have been very extensive compilations of the constants in water, we only need to know the slopes of the Log K's vs. 1/ lines in order to predict. With the exception of the NTA-Co case, all cases give a satisfactory first order approximation, bearing in mind the oversimplification we have made to do the estimations. The radius of Co+2 of 5.76 is derived from [CoCitrateH]/[Co][CitrateH-2] complexation constants, it will be 2.41 if we calculated it from [NTACo]/[NTA][Co] complexation constants, it seems that NTA sees a different Co+2 than citrate or oxalate. Thus we can readily describe the increased stability of metal-ligand complexes in some mixed solvent systems with the Born equation.

The interesting aspect was noticed for Cu-EDTA complexes. The stability constants shopwed little effect of acentone concentration. For CuEDTA-2, the aqueous constant might be used in transport modeling without resulting in large errors.

MeOH-H_2O Solution

Although the approximate linear relationship was also observed for Citrate-Co and EDTA-Co complexes in MeOH-H_2O systems the Born equation could only describe this system of negative ionic radii were utilized. This is obviously not a realistic condition. Therefore the electrostatic interaction, which is the basis to derive the Born equation, does not play a major part . As a result, we used LFER in the prediction of the constants:

$$RT\ (Ln\ Ka\ (m) - Ln\ Ka\ (w)) = -Gm + Gw$$

$$RT\ LnKa = -(G\ (products) - G\ (reactants))$$

$G(H^+)$, G(A), $G(M^{2+})$, etc. n t(H+), n t(A), n $t(M^{2+})$, etc., respectively

Where A stands for ligand with charge omitted for simplicity, n for mole fraction of MeOH, t the LFER parameters. These relationship may be used when linear relation between Log K's and n is observed. We have to make further simplification that t values for neutral species were negligible

compared to those for charged species in order to derive a set of t's and the t for M(II)-ligand equal to that of H_2Ligand. The Gm values for H+ were obtained from [Feakins].

Ions	H+	H_2Citrate$^-$	HCitrate^{2-}	Citrate^{3-}	Co^{2+}	H_3L^-	H_2L^{2-}	HL^{3-}	L^{4-}
t (1/mol)	-6	8.48	17.41	27.69	-12.43	9.59	19.68	27.98	33.87

L means $EDTA^{4-}$. The physical meaning of t's is that a negative value means the ion is more stable in co-solvent than in water, which is the case for most of the cations. The opposite is true for anions. For Oxalate-Co and NTA-Co systems, the LFER does not hold for the last acidic constants for the ligands, so this approach can not be used. The stability of the neutral oxalic acid and NTA is determined by the free energy differences between the products and the reactants. Since the anions are less stable in MeOH-H_2O solution but H^+ is more stable in it, the stability of the products is a trade off between the 2 factors, and among others.

Cu-EDTA showed a slightly decreasing trend with increased methanol content, the 1st acidic stability constants for EDTA-4 are also slightly dropping with the increase of the MeOH in the solutions.

Significance

Our analytical methodology has allowed us to measure the stability constents of selected metal-ligand complexes in mixed solvent systems. As anticipated, a general trent of increasing stability with increased organic cosolvent was observed, but the magnitude of increase was small for complexes with large aqueous stabilities such as Cu-EDTA. The ability to model metal-ligand complexes in acetone-water solutions with the Born equation and in methanol-water solutions with Linear Free Energy Relationships based on the acidity constants, provides a tool that can be extended to future research activities. In the next phase of our research we will extend these measurements to heterogeneous systems containing and adsorbing solid phase. This will allow us to study processes occurring in hazardous and radioactive waste sites.

Publications:

Xue, Y. and S.J. Traina. 1993. Potentiometric tiration and computer-aided refinement techniques for measuring stability constants of multi-basic acids and their complexes with metal ions in semi-aqueous solutions. Agron. Abstr. pg. . 53.

Training:

Xue, Y. M. S. Student in Agronomy.

SYNOPSIS

Project Number: 05

Start: July 1993 (Actual)
End: December 1994 (Expected)

Title: Prediction of Toxicity for Pesticides Found in Ohio Surface Waters

Investigator: S.W. Fisher, Ohio State University

Focus Categories: TS, WQN, SW

Congressional District: 15

Descriptors: Pesticides, Hazard Assessment, Water Quality Standards, Fate Prediction

Problem and Research Objectives: Recent efforts directed toward monitoring the presence of pesticides in Ohio surface waters reveal that 13 pesticides (10 herbicides and three insecticides) are regularly found over the maximum contaminant level (MCL). Several of these pesticides are present, on a seasonal basis, at levels that are high enough to cause acute and chronic toxicity to aquatic oganisms. It is therefore desirable to have available means of predicting under which environmental conditions these compounds are likely to exceed the prescribed MCL and what the likely effects on key aquatic species will be. The research developed predictive models based on the use of Molecular Connectivity and Linear Solvation Energy Requirements for describing the toxicity of insecticides and herbicides under different environmental conditions. Specific research objectives were : 1) To conduct toxicity tests of 10 organophosphorus insecticides on *Chironomus riparius* under varying conditions of pH (6,7 or 8) and temperature (11, 17 or 22°C) and sediment (with and without sediment); 2) Conduct toxicity tests of 10 herbicides on the alga, *Chlorella pyrenoides*, using several different endpoints to gauge toxicity; 3) Calculate LSER and MC indices for each pesticide tested; 4) Perform regression analysis with molecular descriptors and toxicity data.

Methodology: Acute toxicity tests were conducted on C. riparius in systems with and without sediment according to the methods of Lydy et al. (1989). Methods were developed for measuring the toxicity of herbicides to the alga, *Chorella pyrenoides.* These were based on Bennett and Brooks (1989) methods and expanded. The process now includes several endpoints of intoxication including: cell death, cell density and chlorophyll content. LSER parameters were calculated for each chemical by Dr. James Hickey of the National Biological Survey. MC parameters were calculated using a MOLCONN computer program. Regressions were run for toxicity data against each molecular parameter and all possible combinations of it. The level of significance for all measurements was $P<0.05$.

Principal Findings and Significance: The results of this study show several things: 1) The toxicity of insecticides to benthic invertebrates is profoundly affected by changing environmental conditions. Temperature exerted the major influence on toxicity with a rise in temperature causing an increase in toxicity for each chemical tested. Although pH also affected toxicity it was not always in a consist manner. In all probability the effect of pH upon toxicity was realized by altering the stability of the insecticide in water as pH changed. These data show that simply knowing that a compound is present in water is not sufficient for defining a hazard. Rather, it is necessary to know how toxicity will change under site-specific conditions; 2) Regression analyses with insecticides showed that both LSER and MC parameters could be used to describe changes in toxicity for insecticides as a function of pH, temperature and sediment type. Of the two multidimensional descriptors, MC worked better in that r^2 values of 0.95 or greater were achieved for each set of conditions. We are now learning why these parameters work by running regressions with unidimensional descriptors that only encode information about one property of each chemical, e.g. lipid solubility, water solubility, volatility, molecular size etc; 3) All of the endpoints tested in the algal cell bioassay gave us a concentration response from which it was possible to estimate EC^{50}s. While each endpoint gave us usable data, it was evident reduction in chlorophyll content was most sensitive and showed significant changes at lower concentrations. Thus, in terms of protecting aquatic ecosystems, it will be most useful to use changes in chlorophyll content as the criterion for effect; 4) Regressions are now underway to determine whether multidimensional and unidimensional molecular descriptors will be useful in describing toxicity of the herbicides and whether it will afford prediction of these responses in the real world. The collective data set from this project significantly advances our knowledge of quantitative structure-activity relationships for predicting the fate and effects of pesticides. this knowledged will greatly facilitate our ability to predict, *a priori*, under which conditions pesticides released into watersheds will have deleterious effect.

Publications: Hwang, H. (1994). Quantitative Structure-Activity Relationships for Predicting the Fate and Effects of Insecticides in Aquatic Systems with Sediment under Varying Conditions of pH and Temperature.

M.S. Thesis, Ohio State University. Mr. Hwang will defend his thesis during summer quarter, 1994. "Predicting the Toxicity of Pesticides in Aquatic Systems Using Quantative Structure Activity Relationships".

Hwang, H., S.W. Fisher and P.F. Landrum (1994). QSARs for Predicting the Fate and Effects of Insecticides to an Aquatic Invertebrate under Varying Conditions of pH and Temperature.
In preparation for Aquatic Toxicology.

Gupta, R., and S.W. Fisher (1994). MC and LSER Analysis of Herbicide Toxicity to the Alga, Chlorella pyrenoides. In preparation for Aquatic Toxicology.

Training: One M. S. Student in the Department of Etomology, Haejo Hwang; and a Post-Ph.D.in Environmental Science, Rashmi Gupta.

SYNOPSIS

Project Number: 06

Start: July 1993 (Actual)
End: June 1994 (Actual)

Title: The Solubility and Potential for Water Contamination of Arsenic in Coal Combustion Wastes When Used for Coal Mine Reclamation

Investigator: Dr. Terry Logan, Department of Agronomy, The Ohio State University, Columbus, OH

Focus Categories: WQL, HYDGEO

Congressional District: 15

Descriptors: Geochemistry, heavy metals, soil chemistry, water quality

Problem and Research Objectives: Solubility and sorption of arsenic in ettringite, a mineral commonly found in alkaline coal combustion residues. The objectives are:

1. Synthesis of Ettringite
2. Determine the weathering reaction products of ettringite, and
3. Determine the extent of sorption and desorption of Arsenic by ettringite

Principal Findings and Significance: Ettringite is a stable mineral in alkaline pH conditions (above pH of 10.5) and forms from the weathering of alkaline flyashes. This mineral is unstable in low pH conditions and weathers to amorphous Al-oxides/Hydroxides. However, the pH buffering capacity of alkaline coal combustion residue in alkaline pH reduces the dissolution and stabilizes this mineral even in equilibrium with atmospheric carbon dioxide. Thus, formation of ettringite plays a significant role in stabilization of heavy metals in coal combustion waste residue waters.

Experiments were conducted for adsorption and coprecipitation of arsenic in ettringite. Arsenic in the pH stability range of ettringite forms stable oxyanions such as AsO_4^{3-} and $HasO_4^{2-}$. The experiments showed that AsO_4^{3-} has very high affinity for sulfate in the channels of ettringite structure. Protonation of AsO_4^{3-} has no effect on the total amount of sorbed arsenic. More than 90 percent of AsO_4^{3-} was removed from solutions even at the solid solution ratios of $4gL^{-1}$. At low concentrations of aqueous AsO_4^{3-}, some new solids are formed. These new solids are yet to be identified. A detailed abstract on the experimental results is attached.

Arrsenic is insoluble in alkaline coal combustion residues because of its incorporation into the structure of ettringite. Increase in the solubility of Ettringite at low pH is of concern and my release arsenic back into equilibrium waters. However, formation of al-oxides and aluminum-hydroxy sulfates at low pH from incongruent dissolution of ettringite may sorb released Arsenic. In addition, presence of foreign ions such as SI, Mg, and Fe in the structure of ettringite may enhance its stability at low pH conditions. However, this is beyond the scope of this study. Ettringite forming waste materials can be used to treat the alkaline wastewater containing arsenic.

Recent amendments to the Clean Air Act will result in the massive production of alkaline wastes in Ohio from the scrubbing of sulphur dioxide discharged from power plants burning high sulphur coal. These wastes are known as Flue Gas Desulphurization or FGD wastes. These wastes are very alkaline because of the presence of free lime which buffers the pH of equilibrium water around 12.5. Studies are in progress to utilize these wastes to amend the abandoned mine spoil and solve the acid mine drainage problems. In addition to the alkalinity, these wastes contain large concentrations of trace elements of heavy metals of Boron, Arsenic and Chromium. The solubility and mobility of these elements in the amended soils depends on the type of initial mineral phases, and the final reaction products. Though the mineralogy of acid mine spoil and mine drainage is well understood, their interactions with minerals in FGD wastes has not been studied previously; due to a lack of understanding of the minerals that form in FGD wastes. This research project focuses on ettringite one of the dominant mineral phases of alkaline FGD wastes.

Weathering of FGD wastes results in the formation of ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}.24H_2O$ in large quantities. The crystal structure of ettringite consists of columns made up of Ca-Al-hydroxide and inter-column space by sulfate. Sulfate in the channels can be replaced by a variety of oxyanions such as CrO_4^{2-}, SeO_4^{2-} and AsO_4^{3-}. Different cations can also substitute for Ca^{2+} and Al^{3+} in the columns. There are several minerals that are found in nature with the same structure as ettringite, but these minerals have different compositions.

Soil iron and aluminum oxides which are a major sink for many of the trace elements, are less stable in alkaline pH conditions, and increase the potential for environmental degradation. In this type of environmental condition ettringite is most stable, and the the research focused on understanding the solubility, weathering and interactions of ettringite with difference trace metals. This research's experimental design included the synthesis of ettringite; the study of its solubility; the determination of its thermodynamic solubility product constant; its weathering in low pH conditions, and evaluation of its efficiency in controlling the solubility of arsenic.

Water used in all of these experiments was deionized water, collected from Barnstead NANOpure system, boiled to dissolve carbon dioxide, and cooled in a glove box filled with N_2 gas. The chemical analysis of cations was performed on a Perkin Elmer atomic absorption spectrometer fitted with graphite furnace. Sulfate and chloride were measured on Dionex 20001 Basic Chromatography Module. Hydrogen ion activity was measured using an Orion Expandable Ion Analyser EA 940

connected to a Ross pH electrode. All of the labware used in the experiments was made of polypropylene. Replicates were made for all of the samples.

Ettringite was synthesized using the saccharate method in a glove box under nitrate atmosphere. A ten percent Sucrose solution was used to enhance the solubility of CaO. Aluminum sulfate and the sucrose solution containing lime were mixed in stoichiometric proportions and continuously stirred for 48 hours. The precipitated solids were separated after this reaction time by using a centrifuge and washed several times with high pH water. This process removed the excess sucrose and any gypsum that precipitated during the synthesis. The solids were dried in a desiccator filled with N_2 gas, and finely ground until it passed through 200 size mesh. Infrared spectroscopy, X-ray diffraction and t Thermogravimetric analysis were used to characterize the material. The results suggest that it is ettringite and in good agreement with reported literature. These solids were used in the solubility, weathering and sorption studies.

The solubility product constant (K_{sp}) for ettringite was measured by dissolving solid ettringite in deionized water and also by precipitating ettringite from supersaturated solutions using common-ion effect. Equilibrium solutions were speciated using SOILCHEM and MINTEQA2 for all aqueous ions, their activities were measured using Davis Equation. The K_{sp} for ettringite dissolution according to the following congruent dissolution reaction is :

$$Ca_6AL_2\ (SO_4)_3\ (OH)_{12}\cdot 24H_2O \leftrightarrow 6Ca^{2+} + 2Al^{3+} + 3(SO_4^{2-}) + 12OH^- + 24H_2O \quad pKsp\text{--}111.32$$

Weathering reactions for ettringite were carried out in the pH range of 4 to 9.5. Samples were collected for every 0.5 pH unit within this pH range and were analyzed for their chemistry. The precipitated solids were separated using a 0.45μm filter papers, dried in a desiccator and characterized using X-ray Diffraction and Infrared Spectroscopy. The experimental results suggest that ettringite dissolves incongruently below a pH of 10.5 to gypsum and amorphous Al-oxides. However, jurbanite is one of the reaction products at very low pH(<4.0). This system is modeled using SOILCHEM, MINTEQA2, EQ3NR and EQ6; by adopting the measured activities from the experiments and introducing foreign ions such as SI, Fe and Mg. The reaction products were clay minerals, iron oxides, alunite and minerals forming jarosite (a hydrous sulphate of iron and potassium crystallizing in the trigonal system; a secondary mineral in ferruginous ores.)

Experiments were conducted for adsorption and coprecipitation as arsenic in ettringite. Adsorption experiments were conducted at different concentrations of arsenic (100 ngL^{-1}), different solid-to-solution ratios, different pH (at 10.5, 11.5 and 12.5). At all these different conditions sorption was above 90 percent of initial concentrations. Xray Diffraction (XRD) studies showed that the structure changed only at high concentrations (.400 mgL^{-1}) and new minerals were precipitated. These new minerals were not reported before in International Center for Diffraction Data search manual. At low initial concentrations as arsenic, the number of moles of sorbed ASO_4^{3-} was much higher than the released SO_4^{2-}. This suggests that at low concentrations AsO_4^{3-} is simply replacing SO_4^{2-} in the

channels. However, the mode of incorporation of AsO_4^{3-} was not clear at high initial concentrations of arsenic. To better understand the molecular interactions at high concentrations, vibrational spectroscopy (Fourier Transformed Infrared Spectroscopy and Raman Spectroscopy) and Xray Absorption Spectroscopy were used. This study is in progress.

Coprecipitation experiments were conducted to study the mode and extent of AsO_4^{3-} incorporation in ettringite. In these experiments ettringite was allowed to precipitate in the presence of different concentrations of aqueous AsO_4^{3-}. Coprecipitation resulted in more than 97 percent of AsO_4^{3-} removal from the aqueous solutions. However, XRD studies suggest that the structure of AsO_4^{3-} substituted ettringite did not change from that of SO_4^{2-} substituted ettringite, except at very high initial arsenic/sulphur ratios. Different spectroscopic techniques are used to probe the molecular environment of arsenic in the ettringites.

In summary, ettringite is a stable phase in alkaline conditions and is very efficient in the removal of arsenic from contaminated waters. Ettringite forming waste materials can be used to treat the alkaline waste waters containing arsenic. Even if the pH drops below the stability range of ettringite, weathering products of ettringite such as iron oxides and jarosite can incorporate arsenic into their structure and lower the concentrations of arsenic in waste waters.

Publications:

Myneni, S. C. B., T.J. Logan, S. J. Traina, 1994, "Solubility and Weathering of Ettringite in Alkaline Wastes: An Equilibrium and Non-Equilibrium Chemical Speciation Study", (In process).

Myneni, S. C. B., T. J. Logan, S. J. Traina, G. A. Waychunas., 1994, "Vibrational and Xray Absorption Spectroscopic Studies of Interactions of AsO_4^{3-} With Ettringite in Alkaline Environments", (In process)

Myneni, S. C. B., S. J. Traina, T.J. Logan, G. A. Waychunas, 1994. "Vibrational and Xray Absorption Spectroscopic Studies of Interactions of CrO_4^{2-} With Ettringite in Alkaline Environments", (In Process)

Myneni, S. C. B., T. J. Logan, S. J. Traina, G. A. Waychunas,1994. "Vibrational Spectroscopic Study of Hydration Around Oxyanions: Interpretation of Anion-Mineral Surface Interactions", (In process)

Myneni, S. C. B., S. J. Traina, and T. J. Logan, 1994. "Retention of AsO_4^{3-} and CrO_4^{2-} by Ettringite in Alkaline Environments", ACS Nat. Meet, V. 34, No. 1, 525.

Myneni S. C. B., T.J. Logan, and S. J. Traina.,1993. "Arsenic Sorption and Solubility of Ettringite, A Mineral with Potential Application in Immobilization of Oxyanions", Agricultural Abstracts, 323.

Myneni, S. C. B., T. J. Logan, S. J. Traina, and J. Bigham., 1993. "Sorption of Arsenate and Chromate in Ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 24\ H_2O$, and Their Release During Weathering", Clay Mineral Society Symp. Proceedings.

Training: One Environmental Science, Ph. D. Thesis Title: "The Solubility and Potential for Water Contamination of Arsenic in Coal Combustion Wastes When Used for Coal Mine Reclamation".

Information Transfer Activities

The Water Resources Center is housed in the Agricultural Engineering Building on The Ohio State University campus. This location provides daily opportunities to work closely and share ideas with researchers in the College of Agriculture as well as the College of Engineering. It also provides a close working relationship with the OSU Agricultural Engineering Cooperative Extension Service. A series of tasks were continued or initiated to transfer and disseminate information developed by researchers affiliated with the Water Resources Center to a wide range of State, Federal, County and Municipal agencies; to private sector, to the academic community and to private citizens throughout Ohio.

Water Luncheon Seminar

The Water Resources Center continued to co-sponsor bi-monthly Water Luncheon Seminar Programs for the water resources community in Central Ohio. These programs, are developed cooperatively with The Ohio Department of Natural Resources (ODNR), the Ohio Environmental Protection Agency (OEPA), the Soil Conservation Service (SCS), the District Office of the United States Geological Survey (USGS), and the Cooperative Extension Service of The Ohio State University. They continue to attract more than 350 water resources professionals annually from Federal, State, County and Municipal Agencies, the private sector and the academic community. These seminars provide a forum to discuss current state, federal and local water policy issues, problems, programs and research results. In addition to providing speakers for one meeting a year, the Water Resources Center provides the administrative and financial support for the seminars. The Center also provides technical equipment to assist the speakers with their presentations. The programs which were presented during the 1993 series follows.

Water Luncheon Seminar FY 1993

Date	Speaker/Agency	Topic
9/21/93	***Donna Myers*** NAWQA Project Chief Ohio District Office USGS	Lake Erie - Lake St. Clair Drainage National Water Quality Assessment (NAWQA) Study
1/11/94	***Michael Baker*** Supervisor Division of Drinking Waters Ohio Environmental Protection Agency	Ohio's Effort to Develop a Coordinated and Comprehensive Ground Water Protection and Management Program
3/15/94	***Robert Burris*** Water Resources Planning Staff Leader Soil Conservation Service	Toledo Harbor Sediment Management
5/10/94	***Mike Schiefer*** and ***Cindy Crecelius*** Division of Water Ohio Department of Natural Resources	Proposed Floodplain Rules Engineering and Administrative

Other Conferences and Seminars the Water Resources Center Co-Sponsored or Supported in FY 1993

Date	Program	Co-Sponsors
11/9-10/93	*Education Will Keep Our Water Resources Out of Jeopardy*	Water Management Association of Ohio Annual Meeting Water Resources Center
11/18/93	*Wayne Nichols Lecture Series* *Bill Richards, Circleville, Ohio* *Former Secretary of Agriculture*	OSU School of Natural Resources Water Resources Center
3/12/94	*Ohio Water Education Program Training Seminar for Teacher Training to Evaluate National WET Materials - Darby Creek Metro Park*	OWEP - Organizers Water Resources Center
5/12/94	*Geographic Information Systems - Spring Meeting Dayton, Ohio*	Water Management Association of Ohio Water Resources Center

Information Dissemination Activities

The Center continued meeting with the leading water resources officials in the state for the purposes of sharing information on current water management and policy issues; seeking continued support for our water research program and disseminating the information and technology developed through this program and others at the universities throughout the state and region.

The Center, continued publishing its newsletter *WATER* which focuses on Ohio's water research, technology, issues, legislation in process, education and Center activities. This publication has a wide circulation that includes public officials, water managers throughout Ohio, university researchers in Ohio and throughout the nation, as well as the general public. It has been well received. Mrs. Carol Moody, is the editor for the newsletter and the secretary to the Center.

Water Management Association of Ohio (WMAO)

The Water Resources Center continued to be the communication center for the Water Management Association of Ohio (WMAO). This not-for-profit, 230 member, state-wide organization promotes and supports the development, conservation, control, protection and utilization of the water resources of Ohio for all beneficial purposes. It is the only Ohio organization that is solely concerned with managing Ohio's water. The WRC provides staff support, office space and equipment to WMAO as a portion of the information transfer program.

Ohio Water Education Project (OWEP)

The Ohio Water Education Program (OWEP) began in the Fall of 1992 with the Ohio Department of Natural Resources and the Water Resources Center. A Memorandum of Understanding supporting this project has been signed by the Water Management of Ohio/Water Resources Foundation of Ohio, the Ohio Department of Natural Resources, the Ohio Environmental Protection Agency and the Water Resources Center. There are two functions to this program. The first provides a database of water education materials and projects available/on-going in Ohio; a listing of materials and supplies available for the classroom; the lists of people statewide interested in working with teachers to promote water resources education. The second segment of this project is sponsoring the National Water Education Program (National Project WET). This is a national program for students in grades K-12 for interdisciplinary water resources education. Classroom teachers have indicated tremendous interest for this information and classroom materials. More than 120 teachers attended workshops to test the materials. The Water Resources Center sponsored one of the two training seminars for teachers this past year, donated office space, telephone and fax facilities, and provided administrative support. This project is housed at the Water Resources Center and is part of the information transfer program.

The Department of Energy Project

This is a collaborative, pilot project with seven water resources research institutes nationally. The Ohio Water Resources Center and Ohio Technology Transfer Center are the lead agencies in this pilot project. Ohio's role is to produce a database of all technologies currently used that could be adapted or applied to remediation of hazardous and nuclear waste sites, such as the Fernald plant in southwestern Ohio. A SUN work station is operational, and the database is in development as are Internet/Gopher protocols. Other locations will test the technologies, provide education programs on progress and produce documentation on the findings.

Ohio Water Atlas

The Center has continued discussions with the Ohio Department of Natural Resources and the Ohio Environmental Protection Agency, as well as other state agencies and universities to develop a Water Atlas for Ohio.

Coöperative Arrangements

Program Development

A call for pre-proposals for the Fiscal Year 1993 State Water Resources Research Program was mailed to research administrators and qualified faculty investigators at more than 40 private and public colleges and universities throughout Ohio in mid-November, 1992. This announcement contained the research priorities identified for the major water problems in the Great Lakes, Upper Mississippi and Ohio River Basins by the Water Resources Research Institutes in the Region.

The announcement also required interested researchers to request a copy of the Preliminary Proposal Application Form which was to be completed and returned to the Water Resources Center in late January, 1993.

Pre-Proposals/Federal Guidelines

Preliminary Proposal Application Forms were requested by and sent to twenty-three investigators and research administrators at ten colleges and universities in Ohio. Central State University, an Historically Black University, was one of these colleges, but they did not request any pre-proposal information. In addition to the application form, a list of the federal guidelines for the Program was also enclosed.

Evaluation/Selection Procedures

Seventeen pre-proposals from seven universities and colleges throughout the state were submitted for evaluation and consideration. These pre-proposals were subjected to a review by all of the members of the Water Resources Center's Advisory Committee. In addition, these pre-proposals were distributed to the various divisions within the principal state and federal water-related agencies in the State by the representatives of these agencies who serve on the Advisory Committee, requesting that the divisions review the proposals. The four agencies included in this evaluation were the Ohio Department of Natural Resources, the Ohio Environmental Protection Agency, the District Office of the United States Geological Survey and the Agricultural Research Service in the United States Department of Agriculture.

The results of these reviews were presented at a meeting of the Advisory Committee where this panel selected six of the pre-proposals and instructed the Center's Director to request fully developed proposals from the investigators for the Committee's further consideration.

The six selected pre-proposals were developed more fully and were re-submitted for consideration. The proposals were subjected to a technical review by at least three qualified evaluators selected by individual members of the Water Resources Center's Advisory Committee. Many of these evaluators were from state and federal agencies.

The results of these reviews were presented at a meeting of the Advisory Committee and this panel ranked the leading proposals in the order they felt would best meet the needs and objectives of the Water Resources Center's programs. The Advisory Committee then instructed the Center's Director to incorporate as many of these projects as Federal funds would permit into the FY 1993 Program, and to develop a project for information transfer for the Center. There was enough Federal monies to support five projects.

The membership of the Water Resources Center Advisory Committee, which includes representatives from four colleges and ten departments of The Ohio State University and representatives of the principal state and federal water related agencies is included in this report.

Regional Cooperative Initiatives

The five projects selected for this program were compared with the FY 1993 Program synopses of the projects included in the programs of the other Water Resources Institutes in the Great Lakes, Upper Mississippi and Ohio River Basin to ensure that there was no duplication of efforts in the Region's research programs.

The Ohio State University has agreed to continue as a Charter Member of the Ohio River Basin Research and Education Consortium, and the Director of the Water Resources Center will continue to serve as one of the University's three representatives to the Consortium.

The Director has been appointed by the Governor of the State of Ohio to serve in two capacities: (1) As Chair of the Ohio Water Advisory Council for the Department of Natural Resources, Division of Water; (2) as a member of the Governor's Blue Ribbon Task Force on Water Resources Planning and Development. The Mayor of the City of Columbus has appointed him for two years to the Environmental Science Advisory Committee (ESAC) for the city.

Program Management

At least once each quarter, the Director contacts the Principal Investigator on each research and information transfer project to discuss progress made during the quarter and to discuss the next quarters plan of activities. At this same meeting budget details are reviewed and discussed, and necessary operating and reporting procedures to the Water Resources Center and to The Ohio State University Research Foundation's business office are described. Progress Reports or Completion Reports will be prepared for each project by the Principal Investigators and will be used by the Program Director to prepare the Program Final Report.

All of the investigators are urged to publish the results of their findings in the technical literature of their major disciplines and in other journals that are appropriate to the topic of their research. They are also encouraged and invited to present their findings at the Water Luncheon Seminar that is a part

The manuscripts that constitute the project completion reports are first reviewed by the Director of the Water Resources Center. As needed the Director seeks the advice and council of appropriate state, federal and university scientists for methods of enhancing the value of the technical completion reports to the water-related community in the state and in the region.

TRAINING ACCOMPLISHMENTS

The following tabulation shows, by fields of study and training levels indicated, the numbers of individuals participating in projects that were financed in part with this grant.

Training Category	**Training Level**				
Discipline	**Bachelor's Degree**	**Master's Degree**	**Ph. D. Degree**	**Post Ph. D.**	**Total**
College of Biological Sciences					
Entomology Dept.				1	1
College of Engineering			1		1
Civil Engineering Dept.					
College of Food, Agricultural & Environmental Sciences					
Agronomy Dept.		1			
Environmental Sciences		1	1		3
College of Mathematics and Physical Sciences					
Geological Sciences			1		1
		2	3	1	6